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Initial Comparisons between the Advanced Technology Development Gen 2 Baseline Cells and Variant C Cells

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Abstract

The Advanced Technology Development Program is testing a second generation of lithium-ion cells, consisting of a baseline and three variant chemistries. The cathode composition of the Variant C chemistry was altered with an increase to the aluminum dopant and a decrease to the cobalt dopant to explore the impact on performance. However, it resulted in a 20% drop in rated capacity. Also, the Variant C average power fade is higher, but capacity fade is higher for the Baseline cell chemistry. Initial results indicate that the Variant C chemistry will reach end of life sooner than the Baseline chemistry.

Introduction

In conjunction with the Partnership for a New Generation of Vehicles (PNGV) Electrochemical Energy Storage Team, the U.S. Department of Energy (DOE) initiated the Advanced Technology Development (ATD) Program in 1998 to address technical barriers impeding the commercialization of high-power lithium-ion batteries for hybrid electric vehicle applications. These barriers include insufficient calendar life, high production costs, and poor response to abuse scenarios. The ATD program is organized into five program areas: baseline cell development (the first generation of cells), diagnostic evaluations, electrochemistry improvement (the second generation of cells), advanced materials (the third generation of cells), and low-cost packaging. A full description of the program and initial results are provided in Reference 1. (Note: PNGV was superseded by FreedomCAR in January 2002).

Gen 2 Cell Chemistry

The ATD Program is now in the process of aging cells and applying advanced diagnostic techniques to the second generation of cells (referred to as Gen 2). The Gen 2 cells include a baseline cell chemistry and three variant chemistries to explore their impact on cell performance (referred to as Variant A, Variant B, and Variant C). Concurrent testing of the Baseline cells and Variant C cells at the Idaho National Engineering and Environmental Laboratory (INEEL), Argonne National Laboratory (ANL), and Sandia National Laboratories (SNL) is underway. Variants A and B have not yet been manufactured.

The ATD Gen 2 Baseline cells (18650 in size) were manufactured to the following specifications, as developed by ANL [2]:

- **Positive Electrode**
 - 84 wt% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
 - 4 wt% carbon black
 - 4 wt% SFG-6
 - 8 wt% PVDF binder
- **Negative Electrode**
 - 92 wt% MAG-10
 - 8 wt% PVDF binder
- **Electrolyte**
 - 1.2 M LiPF_6 in EC/EMC (3:7 wt%)
- **Separator**
 - 25 μm thick PE Celgard

The Variant C cell chemistry differs from the baseline chemistry by an increase to the aluminum dopant from 5% to 10% and a decrease to the cobalt from 15% to 10% in the cathode (i.e., $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Al}_{0.1}\text{O}_2$).

Table 1: Characterization data for all Baseline and Variant C cells.

| | C₁/1 Capacity | C₁/25 Capacity | EIS at Semi- Circle Trough | PNGV Power | BSF |
|------------------------|-------------------------------------|--------------------------------------|---|-----------------------------------|------------|
| Units | Ah $\pm \sigma$ | Ah $\pm \sigma$ | mΩ $\pm \sigma$ | kW $\pm \sigma$ | |
| Baseline Cells | 0.979 \pm 0.011 | 1.074 \pm 0.013 | 16.97 \pm 0.45 | 32.51 \pm 0.71 | 553 |
| Variant C Cells | 0.826 \pm 0.016 | 0.976 \pm 0.028 | 20.03 \pm 1.13 | 32.57 \pm 1.06 | 651 |

Table 2: Twelve-week data for Baseline and Variant C cells cycled at 45°C and 60% SOC.

| | C₁/1 Capacity | Capacity Fade | C₁/25 Capacity | EIS at Semi-Circle Trough | PNGV Power | Power Fade |
|----------------------------|-------------------------------------|----------------------------------|--------------------------------------|---|-----------------------------------|----------------------------------|
| Units | Ah $\pm \sigma$ | % $\pm \sigma$ | Ah $\pm \sigma$ | mΩ $\pm \sigma$ | kW $\pm \sigma$ | % $\pm \sigma$ |
| Baseline Cells | 0.921 \pm 0.008 | 5.77 \pm 0.42 | 0.981 \pm 0.013 | 20.74 \pm 0.67 | 27.72 \pm 0.58 | 14.19 \pm 0.39 |
| Variant C Cells | 0.801 \pm 0.018 | 3.10 \pm 0.30 | 0.932 \pm 0.028 | 26.20 \pm 0.99 | 26.27 \pm 0.67 | 20.28 \pm 0.45 |

Cell Testing

The ATD Gen 2 cells are being subjected to cycle-life testing at INEEL, calendar-life testing at ANL, and accelerated-life testing at SNL. To the extent practical, all testing is done in accordance with the *PNGV Battery Test Manual* [3].

Life testing is interrupted every four weeks (33,600 cycles) for reference performance testing (RPT), which is used to quantify changes in capacity, resistance, and power. RPT's consist of a C₁/1 static capacity test, a low-current Hybrid Pulse Power Characterization (L-HPPC) test, a C₁/25 static capacity test, and an Electrochemical Impedance Spectroscopy (EIS) test [4]. The RPT that is performed immediately prior to the start of life testing is referred to as characterization. All RPT's are performed at 25°C.

The remainder of this paper focuses on the similarities and differences of the Baseline and Variant C cells tested at the INEEL. INEEL received 30 Baseline cells in early January 2001. These cells were split into two groups of 15, with one group aged at 25°C and the other group at 45°C. Fifteen Variant C cells, which are being aged at 45°C, began testing in mid-August 2001. Cycle-life testing is performed at 60% state-of-charge (SOC).

Cell Performance

Due to a change in the cathode composition, the Variant C cell rated capacity (0.8 Ah) is 20% lower than the Baseline cell rated capacity of 1.0 Ah. As a result, lower currents are used during cycle-life and reference performance testing on the Variant C cells. However, direct comparison between the Baseline and Variant C cell performance is possible through a scaling process called the Battery Size Factor (BSF). The BSF is the minimum number of cells required to simultaneously meet PNGV power and energy goals with a beginning of life power margin of 30% [3].

Table 1 compares the Baseline cell characterization performance to that of the Variant C cells. The table includes averages plus or minus one standard deviation of the C₁/1 and C₁/25 capacities, the EIS real impedance at the semi-circle trough, and the PNGV Power (which is the BSF-scaled cell power at 300 Wh). All 30 Baseline cells were used in the average since cycle-life testing had not yet begun. As shown in Table 1, the Baseline chemistry requires 553 cells to meet PNGV goals and the Variant C chemistry requires 651 cells.

Similarly, Table 2 compares the Baseline cell performance to that of the Variant C cells, but after twelve weeks of cycle-life testing at 45°C. Only the data from the Baseline cells that were cycle-life tested at 45°C were used when calculating the averages. *Capacity fade* is the percent loss in the discharge capacity during the C₁/1 test; *power*

fade is the percent loss in the PNGV Power. The fades are normalized to the characterization RPT.

Capacity - Figure 1 shows the $C_{1/1}$ static capacity results for the 15 Baseline cells tested at 45°C. These cells have been cycling for a period of 32 weeks. Due to the end-of-test (EOT) criteria, some cells have already been removed from testing and sent for diagnostic analyses [4]. Figure 2 shows the $C_{1/1}$ static capacity results for the Variant C cells after 12 weeks of testing (INEEL Cell Number 173 had a manufacturing defect and was removed from test before Characterization). These figures show the uniform and monotonic decline in discharge capacity during life testing. The Baseline cell capacities are larger than the Variant C capacities, but they are also fading more rapidly than the Variant C cells (see Table 2). Similar results are seen for the $C_{1/25}$ capacities.

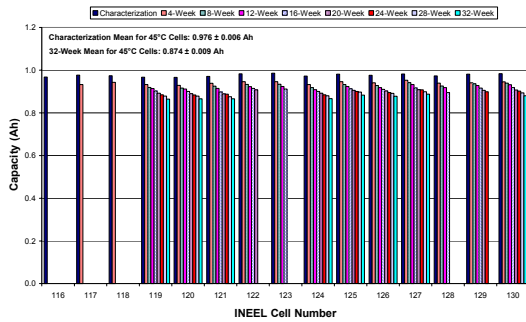


Figure 1: $C_{1/1}$ static capacity for 15 INEEL ATD Gen 2 Baseline cells cycled at 45°C.

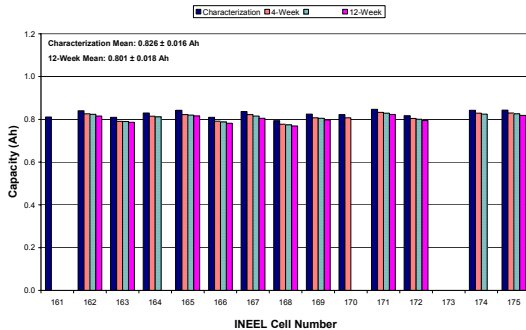


Figure 2: $C_{1/1}$ static capacity for 15 INEEL ATD Gen 2 Variant C cells cycled at 45°C.

A new measure of cell degradation under evaluation by the ATD Program is the differential capacity, Q_{diff} . It is given by $Q_{diff} = (1/Q)[d(Ah)/dV]$, where Q is the group average characterization $C_{1/25}$ capacity. Figures 3 and 4 show the differential capacities for representative Baseline and Variant C cells, respectively, plotted

as a function of voltage. The peaks of the resulting curves are thought to be related to specific intercalation sites within the anode and/or cathode. The peaks for both cell chemistries at characterization occur at approximately the same SOC's (i.e., 10%, 40%, and 80% SOC). The differential capacity for the Baseline cells significantly decreases and shifts to the right as the cells are aged, whereas the Variant C cells are decreasing at a slower rate. This is consistent with the capacity fade mentioned above. The initial charge peak for the Variant C cells at ~5% SOC is lower in magnitude than the Baseline cells, and the initial discharge peak is missing. This indicates that the Variant C cells had more difficulty adding or removing capacity over that voltage interval at the beginning of life, possibly as a result of the 10% aluminum-doped cathode.

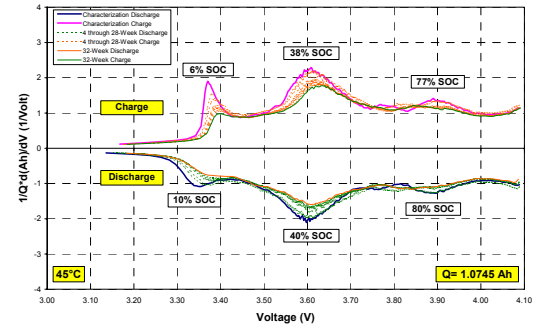


Figure 3: Differential capacity shift for a representative Baseline cell.

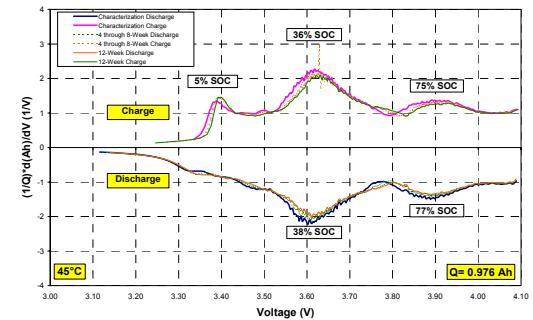


Figure 4: Differential capacity shift for a representative Variant C cell.

Power – Figure 5 shows the BSF-scaled PNGV Power at 300 Wh for the 45°C Baseline cells, and Figure 6 shows the PNGV Power for the corresponding Variant C cells. On average, the Variant C chemistry requires 98 more cells to meet the PNGV power and energy goals compared to the Baseline cell chemistry (see Table 1). Furthermore, the Variant C cells have a higher power fade than the Baseline cells (see Table 2).

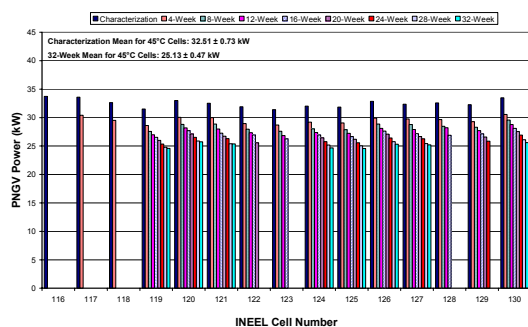


Figure 5: PNGV Power at 300 Wh for 15 INEEL ATD Gen 2 Baseline cells cycled at 45°C.

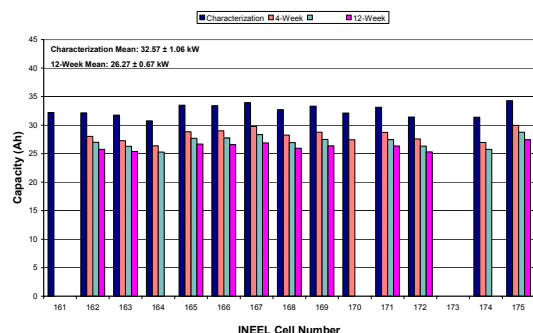


Figure 6: PNGV Power at 300 Wh for 15 INEEL ATD Gen 2 Variant C cells cycled at 45°C.

EIS - The ATD Program is also using EIS testing to investigate cell degradation. Figures 7 and 8 show the EIS Nyquist plots for representative Baseline and Variant C cells, respectively. Changes in the first semicircle (i.e., increases in the real impedance) as the cell ages are related to the growth of a thin film solid electrolyte interface layer on the anode and/or cathode. As shown, the impedance of the Baseline cells is growing at a slower rate. The Variant C cells have both an initially higher impedance, as well as a higher impedance growth rate.

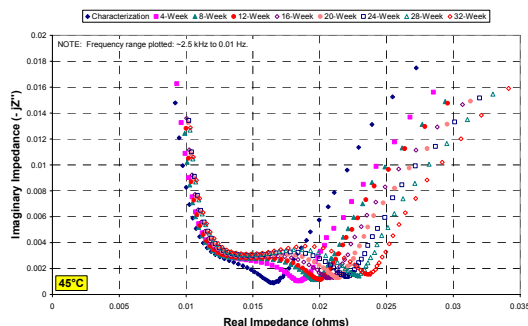


Figure 7: 60% SOC EIS impedance for a representative Baseline cell.

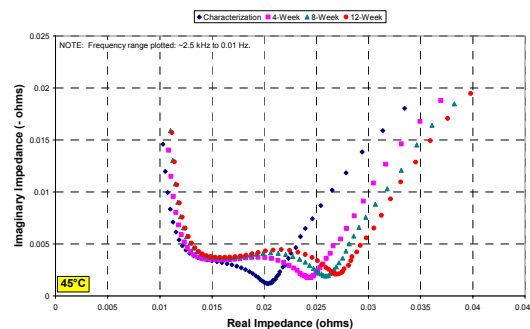


Figure 8: 60% SOC EIS impedance for a representative Variant C cell.

Conclusion

Testing of the ATD Gen 2 Baseline and Variant C cells is underway. Although the rated capacity of the Variant C cells is 20% lower, use of the BSF allows direct comparisons to be made. The $C_{1/1}$ and $C_{1/25}$ capacities are higher for the Baseline cells, but capacity fade is also higher. This is also evident in the differential capacity plots. The power fade is higher for the Variant C cells. This is also seen in the EIS Nyquist plots, where the Variant C cells have a higher rate of resistance growth. These results indicate that the Variant C cells will reach the end of life criteria before the Baseline cells. The increase in aluminum-dopant for the Variant C cells appear to have a deleterious effect on both the initial capacity and the power fade during aging.

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